Novel Iridium Complexes of an Azine Diphosphine: Very Reactive Iridium(i) Species formed by a Unique Isomerisation of an Iridium(III) Hydride. A New Method of creating Coordinative Unsaturation

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The coordinatively saturated iridium(III) hydride \([\text{IrHCl(CO)}(\text{Ph}_2\text{PCH}2\text{C}(\text{Bu})\text{N}−\text{N}−\text{C}(\text{Bu})\text{CH}_2\text{PPh}_2)]\) containing an ene-hydrazone backbone isomerises reversibly in a polar solvent to give the reactive and coordinatively unsaturated iridium(i) salt \([\text{IrHCl(CO)}(\text{Ph}_2\text{PCH}2\text{C}(\text{Bu})\text{N}−\text{N}−\text{C}(\text{Bu})\text{CH}_2\text{PPh}_2)]\) which reacts rapidly with alkenes, acetylenes, dihydrogen, etc.

Coordinative unsaturation is extremely important in transition metal chemistry and associated areas of catalysis; a classic illustration of this is the coordinatively unsaturated \((18e)\) diethylene rhodium(i) complex \([\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}(\text{acac})]\) (acac = acetylacetonate), which exchanges complexed ethylene with free ethylene at \(10^4\) times the rate which the coordinatively saturated \((18e)\) complex \([\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}(\text{t}-\text{C}_6\text{H}_5)]\) exchanges. Here, we describe a new method of generating a labile, coordinately unsaturated complex by the rapid and reversible isomerisation of a coordinatively saturated iridium(III) complex. The isomerisation involves using an ene-hydrazone backbone of a diphosphine ligand as the sink for a hydrogen atom, thereby giving an azine backbone. An azine or ene-hydrazone forms an extremely stable backbone for a diphosphine, is easily prepared, very resistant to hydrolysis, and has not previously been used in this way. Iridium complexes, e.g. Vaska’s complex, trans-[IrCl(CO)(PPPh)]\(_2\) have proved to be excellent model systems for predicting the behaviour of many other tertiary phosphine-metal complexes, including their use in catalysis.

We have shown that the azine diphosphine Z,Z-[Ph_P(Ph-P)(C(Bu)=N-N=C(But)CH2PPh)] cannot chelate through both phosphorus atoms because of the Z,Z-configuration, but can bridge two metal centres to give binuclear or polymeric species. However, rotation around C=N can occur quite readily and the azine diphosphine in the E,Z-configuration can chelate to a metal giving a nine-membered ring or act as a terdentate ligand with \(PP\) and \(N\) donor atoms. We now find that 1 reacts with the labile iridium(i) carbonyl complex [IrCl(CO)(p-toluidine)] to give the coordinatively saturated \((18e)\) iridium(III) hydride 3 (Scheme 1), in which a hydrogen atom has been lost from a methylene carbon and an iridium hydride has formed, presumably by oxidative addition of the N-H bond. This could involve an azine ene-hydrazone tautomerism, i.e. a 1,3-proton shift as shown, \(2a\) ↔ \(2b\). We formulate the stereochemistry of the iridium(III) hydride complex as \(3\), since \(J_{pp}\) is large (312 Hz) and characteristic of trans-phosphines, and the value of \(\delta_1\) (15.4) in the \(^{1}H\) NMR spectrum is close to similar hydride ligands trans to chlorides for a range of iridium(III) hydrides derived from azine monophosphines. Furthermore, oxidative addition of C-H, N-H, S-H, O-H, Si-H, B-H, or H\(_2\) to iridium(i) is usually cis oriented. In general, coordinatively saturated iridium(III) carbonyl hydrides show poor reactivity towards alkenes, e.g. [IrHCl(CO)(PPPh)]\(_2\) or [IrHCl(Ph)Cl(PPPh)] or related species. However, we find that 3 readily dissolves in methanol or ethanol to give an isomeric but coordinatively unsaturated iridium(i) complex salt 4a in which a hydrogen atom has moved back to the methine carbon of the ene-hydrazone backbone and the iridium has lost its hydride ligand. This salt 4a is readily isolated, and on dissolution in benzene or dichloromethane it immediately reverts back to the iridium(III) hydride 3. The interconversion (or isomerisation) 3 ↔ 4a is rapid and can be readily followed by the characteristic \(^{31}P\)\(^{1}H\) NMR, \(^{1}H\) NMR or IR spectra of the two species. Treatment of 4a with \(\text{NH}_2\text{PF}_6\) in methanol gives the corresponding \(\text{PF}_6\) salt 4b.

The salts 4a or 4b rapidly take up unsaturated molecules. A solution of 4a in methanol reacts with ethylene to give 5a; 4b in CD\(_2\)Cl\(_2\) or CH\(_2\)Cl\(_2\) reacts completely with ethylene in a few seconds to give a colourless adduct 5b. The \(^{1}H\)\(^{31}P\) and \(^{1}H\) NMR spectra of 5b show that it is fluxional and most of the resonances are very broad at 25 °C (\(\tau_{1/2} > 10\) Hz). When the CD\(_2\)Cl\(_2\) solution is cooled to −40 °C the resonances become sharp and the four ethylene protons give a well-defined ABMX pattern in the \(^{1}H\)\(^{31}P\) spectrum, and the two CH\(_2\)P protons each give an AX pattern (at 400 or 600 MHz). We have formulated this five-coordinate ethylene complex as a trigonal bipyramid with the ethylene in an equatorial position and the double bond in the equatorial plane of the complex; other five-coordinate alkeno-iridium(i) complexes have the alkene in the equatorial plane.

Scheme 1 Reagents and conditions: i, [IrCl(CO)\(_2\)1-(toluene)]; ii, \(\text{EtOH or MeOH}\); iii, \(\text{C}_2\text{H}_4\) or \(\text{CH}_2\text{Cl}_2\); iv, \(\text{NH}_2\text{PF}_6\); v, \(\text{L}\) or \(\text{NH}_2\text{PF}_6\); vi, for 5b, 5d, 5x, \(\text{Li}\) or \(\text{NH}_2\text{PF}_6\); vii, \(\text{H}_2\); viii, 20 °C, 24 h; ix, \(\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}\).
plane and it has been suggested by Rossi and Hoffmann that this is the preferred structure for five-coordinate iridium(III) alkene complexes.

Allen reacted similarly with 4b to give a mixture of two colourless adducts, in the approximate ratio of 4:1. These are probably complexes analogous to the ethylene complex 5b with the alkenes pointing ‘left’ (5c) or ‘right’ (5d) and are not fluxional at 25 °C. Other alkenes or acetylenes with electron-withdrawing substituents, such as dimethyl fumarate, diethyl fumarate, N-methylmaleimide, dimethyl acetylenedicarboxylate or methyl proprionate, also gave π2-adducts of the type [Ir(CO)2(L)(Ph3P)3Be(C6H5)]−N=N−C(Bu3)2PPh2−PNN] (PF6) (L = alkene, acetylene) which were similarly characterised and probably have structures of type 5.

The iridium(III) salt 4b reacted rapidly with H2 to give an adduct of configuration 6∥ with the phosphorus donor atoms mutually cis and each trans to H. In solution over a period of 24 h, 6 isomerised almost completely to give a dihydride 7∥ with mutually trans-phosphines.

A key step in many organometallic and catalytic reactions is the migration of a hydride ligand from the metal to a coordinated alkene such as ethylene (A → B → C Scheme 2). Examples where this occurs include hydrogenation, hydrodeoxygenation, hydrogen elimination) is also important. For a hydride complex which from preliminary work show a similar behaviour to 1∥, we have made diphosphines from (1R)-(+)-camphor azine, other ketones or aldehydes, including chiral molecules. Thus, studying diphosphines and monophosphines generated from 1∥, 2∥ and EtO2CN=NCOC2H5 has the structure 8∥ in which a hydrogen atom has indeed moved from the phosphine backbone participating in the chemistry by acting as a temporary source and sink for a hydrogen atom.

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Footnotes

∥ New compounds were characterised by elemental analyses, and by IR, 1H{13C}[H] NMR (36.2 MHz) and 13C NMR (100, 400 or 600 MHz) spectroscopy.

∥ Selected NMR and IR data for 3: δp(CD3O) ref. 85% H3PO4 34.3, 3a 20.3, 3J(P/H) 312 Hz, δP(CDC13, TMS) −15.40 [H, dd, 3J(P/H) 10.6, 11.4 Hz, 1H], 4.80 [H, t, 2J(P/H) = 4.9 Hz, PCH2]−4.80 [H, t, 2J(P/H) = 4.9 Hz, PCH2]; IR v/cm−1 (MeOH) v(C=O) 2000. For 4a: δp(MeOH–CD3) 30.6, 3a 20.3, 3J(P/H) 303 Hz; δP(CDC13) 3.48 [H, d, 3J(P/H) 10.0 Hz, CH3], 4.17 [H, dd, 3J(P/H) 7.8, 4J(P/H) 2.5 Hz, CH2]; IR v/cm−1 (CH2Cl2–v(C=O) 2015. For 5b: δP(CDH3CN) 38.4, 3a 10.4, 3J(P/H) 57 Hz; IR v/cm−1 (EtOH) v(C=O) 2015. For 5b: δP(CDH3CN) 38.4, 3a 10.4, 3J(P/H) 57 Hz; IR v/cm−1 (EtOH) v(C=O) 2015. For 5b: δP(CDH3CN) 38.4, 3a 10.4, 3J(P/H) 57 Hz; IR v/cm−1 (EtOH) v(C=O) 2015.

References